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(54) **METHOD FOR THE OXIDATION OF BENZENE AND/OR TOLUENE TO PHENOL AND/OR CRESOLS**

**VERFAHREN ZUR OXIDIERUNG VON BENZOL UND/ODER TOLUOL ZU PHENOL UND/ODER CRESOL**

**PROCEDE D'OXYDATION DE BENZENE ET/OU TOLUENE EN PHENOL ET/OU CRESOLS**

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## Description

## BACKGROUND OF THE INVENTION

- 5 [0001] The present application is a U.S. non-provisional application based upon and claiming priority from Russian Application No. 99106881 which is hereby incorporated by reference.
- [0002] The proposed invention relates to the field of organic synthesis, more specifically to a method for the production of phenol and cresol by the direct selective oxidation of benzene and toluene by means of a gaseous mixture containing nitrous oxide  $N_2O$  in the presence of a heterogeneous catalyst. The catalysts used are zeolite-containing catalysts modified by special treatment and additives.
- 10 [0003] The known method most similar to the proposed method is a means of oxidizing benzene and/or toluene to phenol and/or cresols using nitrous oxide as the oxidizing agent, with a heterogeneous catalyst containing a high-silica pentasil zeolite which is modified in a preliminary step in which metal ion promoters are added by applying a compound of metals such as iron, etc. to it, then activating the catalyst at a high temperature between 300 and 500°C, and bringing the benzene and/or toluene and the nitrous oxide into contact with the modified heterogeneous catalyst at a reaction temperature between 275 and 450°C (U.S. Patent No. 5,110,995, IPC C 07 C 37/60, national code 568/800,1992).
- 15 [0004] In the known method, pentasil zeolites (ZSM-5, ZSM-11, ZSM-12, ZSM-23), mordenite, H-beta zeolite and EU-1 that have been modified with small amounts of iron ions at the zeolite synthesis stage have been shown to be highly active in the direct oxidation of benzene to phenol. At temperatures of 400-450°C and a contact time of 2-4 sec (space velocity in terms of benzene  $0.4\text{ h}^{-1}$ ) and a benzene: $N_2O$  molar ratio of 1:4, the yield of phenol reaches values of 20-30% with a selectivity of 90-97%. Other systems modified with transition metal ions (Mn, Co, Ni, V, Cu), have been shown to be less active than iron-containing zeolites.
- 20 [0005] The disadvantages of the known method are related to the need to introduce the iron into the zeolite and to control the state of the iron ions, the low value of the space velocity in benzene and the quite lengthy contact time necessary to achieve acceptable, but not especially high yields of the final products, as well as the low selectivity achieved at elevated temperatures.
- 25 [0006] DE 196 34 406 A discloses a method for oxidizing aromatic compounds with  $N_2O$  to the corresponding hydroxyaromatic compounds characterized in that the reaction is carried out in the presence of a zeolite catalyst (pentasil or  $\beta$ -type). The zeolite catalyst is previously treated with water vapor at a temperature of from 300-800 °C. The catalyst can also be a metal-containing silicate zeolite, such as a Zn-containing silicate-zeolite. Examples of the aromatic compounds are benzene and toluene as well as their derivatives. Reaction temperatures for the oxidation reaction are from 250 - 550°C.
- 30 [0007] The result produced by the proposed method is an increase in the yield of the final products and an improvement in the selectivity and activity of the catalyst achieved by creating strong Lewis acid sites in the zeolite.

## BRIEF SUMMARY OF THE INVENTION

- [0008] According to this method, a starting material such as benzene or toluene or a combination thereof is oxidized to form phenol, cresols or a combination thereof. The oxidation is performed at a temperature of 225 °C to 500 °C in the presence of a zeolite catalyst and an oxidizing agent which comprises nitrous oxide. The zeolite catalyst is treated according to a special procedure to form the catalyst. Specifically, the zeolite is first calcined at 500 - 950 °C in air or at 300 - 850 °C in an inert gas. Next, the zeolite is impregnated with Zn ions by ion exchange or by exposing it to an aqueous solution of zinc salt. Last, the impregnated zeolite is heated in air or an inert gas to a temperature of 300 - 850 °C.

## DETAILED DESCRIPTION OF THE INVENTION

- [0009] As the high-silica zeolite one can use a pentasil; the pentasil may be the H form of the ZSM-5 zeolite with an Si/Al ratio of 10 to 200.
- 50 [0010] The reagents may be taken in a ratio of  $N_2O$ :benzene and/or toluene from 1:7 to 10:1.
- [0011] Furthermore, the mixture of benzene and/or toluene with nitrous oxide may be diluted with an inert gas - nitrogen and/or argon and/or helium.
- [0012] Furthermore, the heterogeneous catalyst may be used mixed with a binder in the form of silica gel or alumina.
- [0013] The method for oxidizing benzene and/or toluene to phenol and/or cresols is accomplished as follows.
- 55 [0014] The starting materials for the catalyst are commercial forms of the zeolite are:

- (1) the high-silica zeolite ZSM-5

## (2) H-beta zeolite

**[0015]** Commercial zeolite ZSM-5, advantageously with a Si/Al ratio greater than 10 and preferably with a ratio of 40-100, is used. ZSM-5 zeolite is modified with compounds containing Zn ions by ion exchange from nitrates, chlorides and other salts of zinc, or by impregnating it with aqueous solutions of zinc salts. In a preliminary step the zeolite is calcined at 400-950°C in air or an inert gas (under static conditions or in a flow). The indicated temperature ensures the dehydroxylation of the zeolite. The zeolite is then impregnated with an aqueous solution of zinc nitrate with a normality of 0.1N to 2N in an amount sufficient to add zinc oxide at a rate of from 0.1 to 10 wt%.

**[0016]** After impregnation, the zeolite is activated at a temperature of 300-500°C.

**[0017]** This impregnation process may be accomplished in one step or in several steps with intermediate activation at 500-700°C.

**[0018]** Acidic forms of the zeolite may be used to prepare the catalyst. The acidic H form of the high-silica zeolite may be prepared by ion-exchange of the Na form of the zeolite with an aqueous solution of an ammonium salt, a nitrate or chlorite or by treating the Na form of the zeolite with an aqueous solution of an inorganic or an organic acid.

**[0019]** The degree of ion exchange of sodium by ammonia or a proton is from 30 to 100% (most preferable is 50-95%). The Na form of the zeolite can also be used as a starting material for preparing the zeolite containing Zn.

**[0020]** The zeolite is used as a catalyst, either in the pure form or combined with a binder. Amorphous silica gel with a specific surface area of 100-600 m<sup>2</sup>/g or alumina (100-400 m<sup>2</sup>/g) or a mixture thereof is used as the binder. The content of binder in the catalyst is from 5 to 50 wt%, preferably 20-30%.

**[0021]** Nitrous oxide is used either pure, or in a mixture with an inert gas - nitrogen or helium. Aromatic hydrocarbons - benzene and toluene - are used as the substrates for the selective oxidation to phenol and cresols. The substrate is introduced at a rate to give a mixture with N<sub>2</sub>O having a molar ratio of N<sub>2</sub>O:substrate from 1:7 to 5:1, preferably from 1:2 to 4:1. The space velocity for the substrate is from 0.2 to 5 h<sup>-1</sup>, ordinarily 0.5-2 h<sup>-1</sup>. The reaction proceeds at a temperature of 225-500°C. The contact time of the reaction mixture with the catalyst is 0.5-8 sec, normally 1-4 sec. The gases exiting from the reactor are a mixture of the corresponding phenols and heavy products that are separated and analyzed by analytical methods. The catalyst may be easily and reversibly regenerated by calcining at 400-600°C in a flow of air, oxygen, nitrous oxide, or in a mixture of these gases in inert gas for a period of 1-3 hours.

## EXAMPLES

## Example 1.

**[0022]** 10 grams of HZSM-5 zeolite are calcined at 900°C in a flow of air for 3 hours and are modified by being impregnated to the zeolite's moisture-holding capacity with an aqueous solution of 1N zinc nitrate. The amount of zinc nitrate added amounts to 2 wt% zinc oxide, obtained on decomposition. The resulting zeolite is then activated at 780°C for 2 hours to convert the nitrate to zinc oxide in the zeolite channels. 1 gram of catalyst with 2% ZnO/HZSM-5 (Si/Al=21), particle size 0.2-0.5 mm, is mixed with 1 gram of quartz of the same particle size and placed in a quartz or steel reactor, i.d. 7 mm. Prior to reaction, the catalyst is activated in an air flow (60 ml/min) at a temperature of 450°C for 1 h. The reaction is run under the following conditions: T=450°C, N<sub>2</sub>O:C<sub>6</sub>H<sub>6</sub> = 1:1, space velocity of benzene V = 0.3 h<sup>-1</sup>.

## Example 2.

**[0023]** The catalyst was prepared as in Example 1. The reaction was run at T=440°C, N<sub>2</sub>O:C<sub>6</sub>H<sub>6</sub> = 0.5:1, V = 0.5 h<sup>-1</sup>. The yield of phenol was 39% with a selectivity of 98%.

## Example 3.

**[0024]** The catalyst was prepared as in Example 1, except that the HZSM-5 catalyst was activated at 600°C. The reaction was run at T=440°C, the benzene was delivered at V = 0.5 h<sup>-1</sup> at a molar ratio N<sub>2</sub>O:C<sub>6</sub>H<sub>6</sub> = 0.5:1. The yield of phenol was 35% with a selectivity of 99%.

## Example 4.

**[0025]** The catalyst was prepared as in Example 1, except that the catalyst used and the calcining temperature required to dehydroxylate the starting H form of the zeolite differed. The zeolite used was 2% ZnO/ H-beta (Si/Al=25) and it was calcined at 800°C. Reaction conditions: V=1.7 h<sup>-1</sup>, N<sub>2</sub>O:C<sub>6</sub>H<sub>6</sub>=1:7. The results are shown in Table 1.

Table 1.

Yield of phenol from benzene oxidized over 2% ZnO/H-beta zeolite (calculated for N <sub>2</sub> O) (V=1.7 h <sup>-1</sup> , N <sub>2</sub> O:C <sub>6</sub> H <sub>6</sub> =1.7)			
Catalyst	Reaction temperature, °C		
	420	440	460
ZnO/H-beta	27.3	38.5	38.0

## Example 5.

[0026] Catalyst prepared as in Example 1 is loaded into a 1-cm<sup>3</sup> reactor (particle size 1-2 mm). Toluene is delivered at V=0.25 h<sup>-1</sup> at a molar ratio of N<sub>2</sub>O:toluene = 1:1. The reaction temperature is 425°C, the yield of a mixture of o-, m-, p-cresols is 21.1% with selectivity for cresol of 75%. Benzene, xylene, and phenol are the major by-products. The ratio of o-, m-, and p-cresols is 30:40:30.

[0027] The examples cited above of the use of a Zn-containing high-silica zeolite catalyst in the oxidation of benzene and toluene to the corresponding phenols with nitrous oxide being used as the oxidizing agent demonstrate the following advantages compared to known catalysts:

1) The rate of conversion over the given catalyst may be increased to 50-77% with no reduction in selectivity (98-100%).

2) The stability of the catalyst is increased by adding zinc ions or zinc oxide, which act as strong Lewis acids, to HZSM-5 zeolite.

3) High activity and selectivity are achieved in the oxidation of toluene by nitrous oxide over Zn-containing zeolite catalyst.

[0028] While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

## Claims

1. A method for oxidizing a starting material selected from the group consisting of benzene, toluene and combinations thereof, to an oxidation product selected from the group consisting of phenol, cresols and combinations thereof, wherein the oxidizing agent comprises nitrous oxide, and said oxidation is performed in the presence of a Zn ion impregnated zeolite catalyst wherein the zeolite has been

- calcined at a temperature of from 500 - 950 °C in air or at 300 - 850 °C in an inert gas,
- impregnated with Zn ions by ion exchange or by exposing the zeolite to an aqueous solution of a zinc salt, and
- activated by heating the impregnated catalyst in air or an inert gas to a temperature of 300 - 850 °C,

wherein the reaction is performed by contacting the starting material with the catalyst in the presence of nitrous oxide at a temperature of 225 to 500 °C.

2. A method according to claim 1, wherein the zeolite is pentasil.

3. A method according to claim 1, wherein the zeolite is pentasil and is the H form of ZSM-5 zeolite with an Si/Al ratio of from 10 to 200.

4. A method according to claim 1, wherein the reagents are taken at a ratio of N<sub>2</sub>O:benzene and/or toluene from 1:7 to 10:1.
5. A method according to claim 1, wherein the mixture of benzene and/or toluene with the nitrogen oxide is diluted with an inert gas-nitrogen and/or argon and/or helium.
6. A method according to claim 1, where the catalyst is used in a mixture with a binder in the form of silica gel or alumina.

#### Patentansprüche

1. Verfahren zum Oxidieren eines Ausgangsmaterials ausgewählt aus der Gruppe bestehend aus Benzol, Toluol und Mischungen daraus, zu einem Oxidationsprodukt ausgewählt aus der Gruppe bestehend aus Phenol, Kresolen und Mischungen daraus, wobei das Oxidationsmittel Distickstoffoxid umfasst und die Oxidation in Gegenwart eines Zn Ion imprägnierten Zeolithkatalysators durchgeführt wird, wobei das Zeolith
  - a) bei einer Temperatur von 500 - 950°C in Luft oder bei 300 - 850°C in einem inerten Gas kalzinert worden ist,
  - b) mit Zn Ionen mittels Ionenaustausch oder dadurch, dass man das Zeolith einer wässrigen Lösung eines Zinksalzes aussetzt, imprägniert worden ist, und
  - c) durch Erhitzen des imprägnierten Katalysators in Luft oder einem inerten Gas auf eine Temperatur von 300 - 850°C aktiviert worden ist,wobei die Reaktion dadurch ausgeführt wird, dass man das Ausgangsmaterial mit dem Katalysator in Gegenwart von Distickstoffoxid bei einer Temperatur von 225 - 500°C kontaktiert.
2. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das Zeolith Pentasil ist.
3. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das Zeolith Pentasil ist und dass es die H Form von ZSM-5 Zeolith mit einem Si/Al Verhältnis von 10 - 200 ist.
4. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** man die Reagenzien in einem Verhältnis von N<sub>2</sub>O : Benzol und/oder Toluol von 1 : 7 bis 10 : 1 nimmt.
5. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** man die Mischung von Benzol und/oder Toluol mit dem Stickstoffoxid mit einem inerten Gas-Stickstoff und/oder Argon und/oder Helium verdünnt.
6. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der Katalysator in einer Mischung mit einem Bindemittel in Form von Silica-Gel oder Aluminiumoxid eingesetzt wird.

#### Revendications

1. Procédé d'oxydation d'une matière première choisie parmi le benzène, le toluène et leurs mélanges, en un produit d'oxydation pris parmi le phénol, les crésols et leurs combinaisons, procédé dans lequel l'agent oxydant comprend de l'oxyde nitreux et on réalise ladite oxydation en présence d'un catalyseur du type zéolite imprégnée d'ions Zn, zéolite qui a été :
  - a) calcinée à une température de 500 à 950°C dans l'air ou à une température de 300 à 850°C dans un gaz inerte,
  - b) imprégnée d'ions Zn par échange d'ions ou par exposition de la zéolite à une solution aqueuse d'un sel de zinc, et
  - c) activée par chauffage du catalyseur imprégné à une température de 300 à 850°C dans l'air ou dans un gaz inerte,la réaction étant réalisée par mise en contact de la matière première avec le catalyseur, en présence d'oxyde nitreux, à une température de 225 à 500°C.

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2. Procédé selon la revendication 1, dans lequel la zéolite est une zéolite pentasil.
3. Procédé selon la revendication 1, dans lequel la zéolite est une zéolite pentasil et est la forme H de la zéolite ZSM-5, ayant un rapport Si/Al de 10 à 200.
- 5 4. Procédé selon la revendication 1, dans lequel les réactifs sont utilisés suivant un rapport  $N_2O$  : benzène et/ou toluène de 1 :7 à 10 :1.
- 10 5. Procédé selon la revendication 1, dans lequel le mélange de benzène et/ou de toluène et d'oxyde nitreux est dilué avec un gaz inerte qui est de l'azote et/ou de l'argon et/ou de l'hélium.
6. Procédé selon la revendication 1, dans lequel le catalyseur est utilisé en mélange avec un liant sous la forme de gel de silice ou d'alumine.

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